

## Electrodeposition of Zinc-Nickel Alloy

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Studies on the electrodeposition of zinc-iron group alloys are of academic and technological interest. The anomalous codeposition and enhanced corrosion protection of zinc-nickel alloy deposits make the search for newer plating bath formulations. Zinc and nickel were codeposited from sulphamate bath and 82 per cent zinc was obtained in the deposit. The sulphamate bath developed offered 100 per cent current efficiency with 24 per cent throwing power.

**Keywords:** Electrodeposition, Zinc, Nickel, Zinc-Nickel alloy

### Introduction

Studies on the development of zinc-transition metal electrodeposits are of technological and academic interest. The codeposition of iron group metals with zinc or with each other exhibit anomalous behaviour; the retardation of the more noble metal by zinc<sup>1</sup>. Zinc-nickel coatings offer enhanced corrosion protection to steel than cadmium<sup>2</sup>. Zinc-nickel electrodeposition from various bath formulations was attempted<sup>3,4</sup>. Sulphate baths in the pH range 1.5 to 2.5 and pH 4 with addition of boric acid and *p*-toluene sulphonic acid were used. Sulphate-sulphamate combinations produced a wide range of zinc-nickel deposits. Chloride baths with SrSO<sub>4</sub> gave bright deposits<sup>5</sup>. Boric acid added acetate baths offered > 15 per cent of nickel. The present investigation deals with the sulphamate bath developed to obtain 12-18 per cent by weight of nickel.

### Experimental Procedure

Cold-rolled steel plates (10 × 7.5 × 0.05 cm) were degreased with trichloroethylene and alkaline electrocleaned cathodically for 2 min in a solution composed of 35 g/L NaOH, and 25 g/L Na<sub>2</sub>CO<sub>3</sub> at 70° C; they were washed in running water, and then dipped for 10s in 5 per cent H<sub>2</sub>SO<sub>4</sub> solutions. Finally, thorough washing and drying were carried out. A Hull Cell was employed to assess and optimize the conditions for the production of good deposits. A cell

current of 1 A was used for 10 min. A regulated power supply was used as direct current source and a calibrated ammeter along with the cell constituted the electrical circuit.

For current efficiency experiments the electrodeposition assembly comprised of electrolytically pure zinc or nickel anodes and steel cathodes of equal size (5 × 4 × 0.025 cm) immersed in a 800 mL solution in a 1 L wide-mouthed glass vessel. The solution was agitated and when necessary heated, using a heater-cum-magnetic stirrer. For current efficiency determination, each specimen was weighed before and after plating and the weight of the deposits was found from the difference.

Current efficiency (per cent) =

$$\frac{\text{Weight of the metal deposited}}{\text{Theoretical weight obtained from Faraday's law}} \times 100, \quad \dots(1)$$

The current efficiency of the alloy is calculated as:

Current efficiency, per cent =

$$\frac{M \times 100}{e_{\text{alloy}} \times Q}, \quad \dots(2)$$

where *M* is the mass of the alloy deposit, *e*<sub>alloy</sub> is the electrochemical equivalent of the alloy and *Q* is the quantity of electricity passed (As).

The electrochemical equivalent of the alloy was calculated as:

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$$e_{\text{alloy}} = \frac{e_{\text{Ni}} \times e_{\text{Zn}}}{(e_{\text{Ni}} f_{\text{Zn}}) + (e_{\text{Zn}} f_{\text{Ni}})} \quad \dots (3)$$

where  $e_{\text{Ni}}$  and  $e_{\text{Zn}}$  are the electrochemical equivalents of the constituent metals;  $f_{\text{Ni}}$  and  $f_{\text{Zn}}$  are their fractions in the deposits. The density of the alloy was calculated by taking into consideration the fraction of the constituent metals. The electrodeposits were removed chemically by immersion in 1:1  $\text{HNO}_3$  and the resulting solutions containing zinc and nickel were analyzed. The amount of nickel in the deposit was calculated from the difference in the mass of the deposit and that of the zinc determined. Zinc content in the solution was analyzed, both volumetrically and by Atomic Absorption Spectrometry.

Throwing power is the ability of the plating solution to deposit uniformly all over the cathode surface and is measured as the ratio of the weight of the deposit obtained on the cathode placed near the far end from the anode.

For determining the throwing power, a Haring and Blum Cell was used. A rectangular cell with two sheet metal cathodes measuring  $9 \times 0.1$  cm, filling the entire cross-section at both ends and a perforated anode of the same area was used. The anode was

placed between the cathodes so that its distance from one of the cathodes was 1/5 of its distance from the other.

$$\text{Throwing power (per cent)} = \frac{K-C}{K+C-2} \times 100, \quad \dots (4)$$

where  $C$  is the metal distribution ratio between the nearer cathode and the farther;  $K$  is the ratio of the distances respectively, of the farther and nearer cathodes from the anode.

Zinc sulphamate was prepared by dissolving zinc oxide in sulphamic acid (99 per cent purity). The nickel sulphamate (99 per cent purity) was supplied by LOBA Chemie, India. The chemicals used in the preparation of the plating bath were of AR quality.

## Result and Discussions

### (a) Zinc and Nickel Deposition

Zinc was deposited on mild steel from sulphamate bath at  $30^\circ \text{C}$ , using a zinc anode. The current efficiencies were found to increase with pH and current density (Table 1). The current efficiency was found to decrease with current density when

Table 1—Influence of pH and current density on the current efficiencies of zinc and nickel from their respective sulphamate baths current efficiency, per cent

Current density A/dm <sup>2</sup>	Zinc deposition at $30^\circ\text{C}$ - $50^\circ\text{C}$		Nickel deposition
	pH 3	pH 4	pH 5.5
1	—	—	100.0
2	96.8	98.8	100.0
3	97.5	98.7	99.0
4	97.8	98.4	98.5
5	98.6	99.2	98.0
6	—	—	96.0
7	—	—	92.0
Zinc bath composition	: Zinc oxide : 133.9 g/L		
	: Sulphamic acid : 81.1 g/L		
	: Boric acid : 10.0 g/L		
Nickel bath composition	: Nickel sulphamate : 250.0 g/L		
	: $\text{NiCl}_2$ : 25.0 g/L		
	: NaF : 4.0 g/L		
	: Beta naphthalene sulphonate 0.345 g/L		

nickel was deposited at 50 °C from sulphamate-chloride bath using Ni anodes. As it was possible to deposit zinc and nickel from sulphamate bath at pH 5.5, detailed investigations were done.

### (b) Alloy Deposition

#### (i) Cathodic Polarization

The variation of mild steel cathode potentials at different current densities in sulphamate baths of zinc and nickel individually are given in Figure 1. The individual cathodic polarization curves do not intersect even at high cathodic potentials. The polarization curves obtained in the alloy plating bath were found to lie between the two individual polarization curves.

#### (ii) Nature of the Deposit

Well known brighteners and leveling agents were used to improve the quality of the deposit. Boric acid,  $\beta$ -naphthol and sodium lauryl sulphate (SLS) at various combinations were tried. Table 2 summarizes the nature of the deposits obtained in the presence of various additives. Grey, uniform, semi-bright deposits were seen only in the presence of boric acid, SLS and  $\beta$ -naphthol.

#### (iii) Current Efficiencies

The amount of nickel deposited in the alloy was found to vary with temperatures and current densities (Figure 2) and a maximum of 38 to 40 per cent nickel was obtained at 50° C. The current density variations

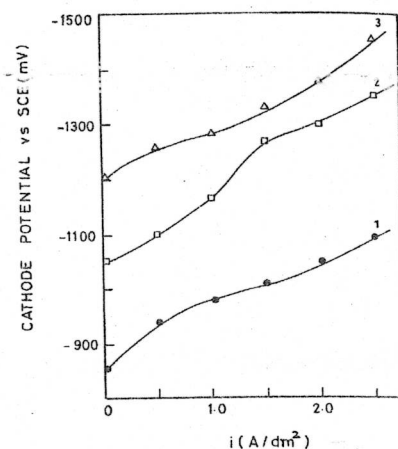


Figure 1— Variation of cathode potentials with current densities in sulphamate baths of zinc-nickel and zinc-nickel alloy at 50 °C -O-O-O- Ni bath - $\Delta$ - $\Delta$ - $\Delta$ - n bath - $\square$ - $\square$ - $\square$ - Zn-Ni bath

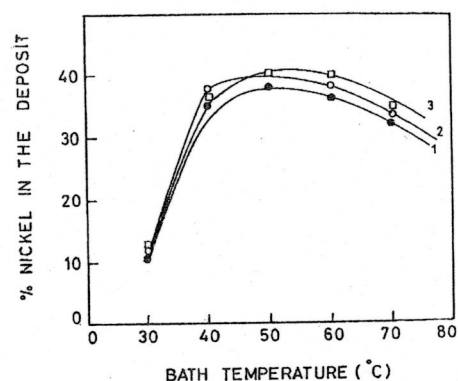


Figure 2 — Influence of temperature on the amount of nickel in the alloy -O-O-O- 1 A/dm<sup>2</sup> - $\Delta$ - $\Delta$ - $\Delta$ - 2 A/dm<sup>2</sup> - $\square$ - $\square$ - $\square$ - 3 A/dm<sup>2</sup>

Table 2 —Effect of addition of addition agents on the nature of the Zn-Ni deposit

Addition agents	Nature of the deposit
No addition agent	Bright, pitted
Boric acid – 50 g/L	Semibright, less pitting
0.345 g/L - $\beta$ - naphthol	Semibright, uniform, milky, less pitting
0.865 g/L sodium lauryl sulphate (SLS)	White and black patches, but levelled
0.345 g/L $\beta$ - naphthol + 0.865 g/L SLS	Milky, but with patches
Boric acid 50 g/L+ $\beta$ - naphthol 0.345 g/L	Semibright, with pits at random
Boric acid 50 g/L+ 0.865 g/L SLS	Milky, uniform grey
Boric acid 50 g/L + 0.865 g/L SLS+ 0.345 g/L $\beta$ - naphthol	Grey, uniform, semibright
Bath :	Zinc sulphamate : 128.6 g/L
	Nickel sulphamate : 125.05 g/L
PH	: 5.5
Temperature	: 50°C
Current density	: 1 A/dm <sup>2</sup>
Stirring	

did not markedly influence the current efficiencies of both zinc and nickel deposition in the alloy (Table 3). The high zinc content in the alloy is anomalous deposition, is due to the formation of zinc hydroxides at the interface. X-ray diffraction and microhardness data obtained on zinc-nickel deposits revealed the inclusion of  $\text{Zn}(\text{OH})_2$  and the existence of a less noble  $\delta\text{Ni}_3\text{Zn}_{22}$  phase which hindered the deposition of nickel<sup>6</sup>. Factors which affected the hydrogen evolution and  $\text{OH}^-$  ion precipitation influenced the composition and the properties of the deposit. A decrease in pH generally causes a decrease in efficiency and improvement in appearance. SLS and  $\beta$ -naphthol might have been adsorbed on the OH ion covered surface and prevented hydrogen evolution.

Boric acid used in Ni-Fe deposition earlier<sup>7,8</sup> did not show any evidence of buffering. Nickel complexed with boric acid might have adsorbed on the  $\text{Zn}(\text{OH})_2$  surface, favouring the enrichment of zinc which caused a grey appearance. Figure 3 presents the effect of  $\text{NH}_4\text{Cl}$  addition in the bath on the current efficiency of the alloy deposition and the weight per cent in the deposit. Introduction of  $\text{NH}_4\text{Cl}$  caused the formation of  $\text{ZnCl}_2$  and  $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$  in the deposit<sup>1</sup>. To get zinc-rich deposit (Table 4) 60 g/l  $\text{NH}_4\text{Cl}$  was found to be optimum. To have an optimum zinc weight percentage (13-18 per cent) the bath with 128.6 g/L sulphamate and 125.05 g/L nickel sulphamate is found to be suitable.

#### (iv) Throwing Power

The Throwing power of the optimized bath was evaluated using zinc and nickel anodes of purity 99.99 per cent. The maximum throwing power was observed at  $1.5 \text{ A/dm}^2$ . When zinc anode was used, the throwing power of the bath varied from -0.5 to 24 in the current density range of  $0.5\text{-}1.5 \text{ A/dm}^2$ . After  $1.5 \text{ A/dm}^2$  there was a decrease in the throwing power from 24 to 9.6. When nickel anode was used, the

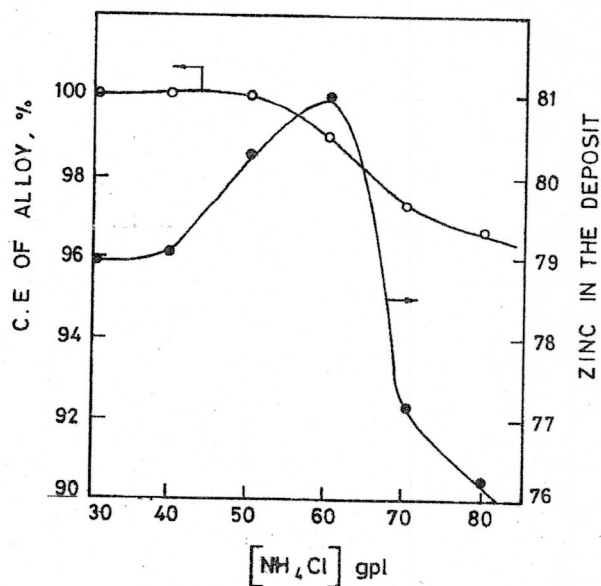


Figure 3 — Effect of  $\text{NH}_4\text{Cl}$  on the current efficiency of alloy deposition and the weight per cent of zinc in the deposit

Table 3 — Influence of the current density on the current efficiencies of Zn-Ni alloy Obtained from sulphamate bath

Current density $\text{A/dm}^2$	Current efficiency, per cent		
	Zinc-nickel Alloy	Zinc	Nickel
0.5	99.02	60.96	38.16
1.0	96.77	59.49	37.98
1.5	98.29	60.43	37.86
2.0	97.16	60.00	37.16
2.5	97.90	60.19	37.70

Bath composition and conditions:

Bath :	Zinc sulphamate	:	128.6 g/L (0.5M)
	Nickel sulphamate	:	125.05 g/L (0.5M)
	Boric acid	:	50.0 g/L
	$\beta$ - naphthol	:	0.345 g/L
	Sodium lauryl sulphate	:	0.865 g/L
	Temperature	:	50°C
	Stirring	:	

Table 4 — Effect of 60 g/L  $\text{NH}_4\text{Cl}$  on the weight percentage of zinc in the deposit

Composition of the bath

Per cent zinc

Without  $\text{NH}_4\text{Cl}$  in solutionWith  $\text{NH}_4\text{Cl}$  in solution

Zinc sulphamate	231.57 g/L
Nickel sulphamate	25.01 g/L
Zinc sulphamate	192.97 g/L
Nickel sulphamate	62.52 g/L
Zinc sulphamate	128.65 g/L
Nickel sulphamate	125.05 g/L
Zinc sulphamate	64.32 g/L
Nickel sulphamate	187.56 g/L
Zinc sulphamate	25.73 g/L
Nickel sulphamate	225.08 g/L

71

81

77

88

65

82

78

90

68

80

Other bath constituents:

Boric acid	:	50 g/L
SLS	:	0.865 g/L
$\beta$ -naphthol	:	0.345 g/L

throwing power of the bath varied from -0.5 to 17.0, in the current density range of 0.5 to 1.5 A/dm<sup>2</sup>. After 1.5 A/dm<sup>2</sup>, there was a decrease in the throwing power from 17.0 to 6.8.

#### (v) Bath Analysis

The electrodeposition was carried out using zinc anodes and the amounts of zinc and nickel contents in the optimized bath were analysed using Atomic Absorption Spectroscopy. The nickel content was found to gradually reduce with time, while the zinc content increased up to 1h and thereafter decreased. This was due to the passivation of zinc anodes with prolonged electrolysis.

#### Conclusions

The optimized bath composition for alloy deposition is zinc sulphamate 128g/L; nickel sulphamate 125.05g/L; boric acid 50 g/L;  $\beta$ -naphthol 0.345 g/L; Sodium lauryl sulphate 0.864 g/L;  $\text{NH}_4\text{Cl}$  60g/L; temperature 50°C with stirring. The bath offered a current density of nearly 100 per cent with a

throwing power of 24 per cent and 82 per cent zinc in the deposit.

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